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CHARGE AND SPIN FLUCTUATIONS Cu^{2+} (S=1/2) ↔ Cu^{3+} (S=1) IN HTSCs. NEW MODEL OF NARROW IMPURITY BANDS

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The energy band of oxide superconductors is theoretically investigated when charge and spin fluctuations of Cu^{2+} (S=1/2)-O^- (S=0) ↔ Cu^{3+} (S=1)-O^{2-} (S=1/2) take place. It is shown that two narrow bands arise near Fermi level under hole doping. The dynamic admixture of $3z^2$-r^2 state to the x^2-y^2 state is equal to approximately 10%.

The Cu^{2+}:$3d^9$ configuration contains one hole in the 3d-shell. Extra holes in CuO_2 planes are added in HTSC materials and the equilibrium Cu^{3+}-O^{2-} ↔ Cu^{2+}-O^- takes place[1]. At present it is not clear what Cu^{3+} states are situated near Fermi level: high spin (S=1) or low spin (S=0) ones.

The goal of this paper is to calculate the structure of energy bands of normal phase CuO_2 planes assuming that high spin copper states are more favourable than low spin ones.

It is known that holes occupy copper states of x^2-y^2 symmetry in dielectric phase of metal oxides. Extra holes due to doping may occupy only states of the system with higher energy. These are either oxygen states or copper states[2]. Let us write down the Hamiltonian as follows

$$H=\sum \varepsilon_1 a^+_{f\sigma}a_{f\sigma}+\sum \varepsilon_2 b^+_{f\sigma}b_{f\sigma}+\sum \varepsilon_j c^+_{j\sigma}c_{j\sigma}$$
$$+\frac{1}{2}I_{11}\sum n^{(1)}_{f\sigma}n^{(1)}_{f\sigma}+I_{12}\sum n^{(1)}_{f\sigma}n^{(2)}_{f\sigma} \qquad (1)$$
$$+K_{12}\sum a^+_{f\sigma}b^+_{f\sigma'}a_{f\sigma'}b_{f\sigma}+\sum t_{jj'}c^+_{j\sigma}c_{j'\sigma}$$
$$+\sum t^{(1)}_{fj}(a^+_{f\sigma}c_{j\sigma}+c^+_{j\sigma}a_{f\sigma})+\sum t^{(2)}_{fj}(b^+_{f\sigma}c_{j\sigma}+c^+_{j\sigma}b_{f\sigma}).$$

Here 1 (2) - the energy of holes in copper states x^2-y^2 ($3z^2$-r^2) respectively, ε_j - the energy of oxigen holes with σ symmetry, I_{11} (I_{22}) - the energy of Coulomb reepulsion for holes in the states x^2-y^2 ($3z^2$-r^2), I_{12} and K_{12} - Coulomb and exchange integrals for holes in the states x^2-y^2 and $3z^2$-r^2, respectively. Creation operators a^+, b^+ and c^+ refer to holes in copper states x^2-y^2, $3z^2$-r^2 and oxygen, respectively. Indices f and j numerate the sites of copper and oxygen.

It is convenient to analyse the energy bands starting from the case when $t^{(1)}=t^{(2)}=0$. The energy operator for copper holes is diagonalised using Hubbard operators $X^{p,q}$. Eigenfunctions of the total hole spin are chosen as basis functions |p> and |q>, for example

$$|\sigma_1,\sigma_2>=b^+_\sigma a^+_{1\sigma_2}|v>,\ |10>=\frac{1}{\sqrt{2}}\sum b^+_{\sigma_1}a^+_{\bar\sigma_2}|v>, \qquad (2)$$

where |v> is the Cu^+ ground state.

There are eight Hubbard sub-bands. The energy sub-bands are given in the Table. The numerical estimates of energies are given relatively to the Hubbard sub-band E_3. They are obtained based on the spectroscopic data [3].

Table. Energy Hubbard sub-bands

$X^{p,q}$	Expression	E in eV
$X^{\sigma_2,\sigma_2\bar\sigma_2}$	$E_8=\varepsilon_2+I_{22}$	4.3
$X^{\sigma_1,\sigma_1\bar\sigma_1}$	$E_7=\varepsilon_1+I_{11}$	3.4
$X^{\sigma_1,00}$	$E_6=\varepsilon_2+I_{12}+K_{12}$	3.4
$X^{\sigma_2,00}$	$E_5=\varepsilon_1+I_{12}+K_{12}$	2.2
$X^{\sigma_1,\sigma_1\sigma_2},X^{\sigma_1,10}$	$E_4=\varepsilon_2+I_{12}-K_{12}$	1
$X^{\sigma_2,\sigma_1\sigma_2},X^{\sigma_2,10}$	$E_3=\varepsilon_1+I_{12}-K_{12}$	0
X^{v,σ_2}	$E_2=\varepsilon_2$	-4.5
X^{v,σ_1}	$E_1=\varepsilon_1$	-5.5

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